

PATENT SPECIFICATION

(11)

1 521 579

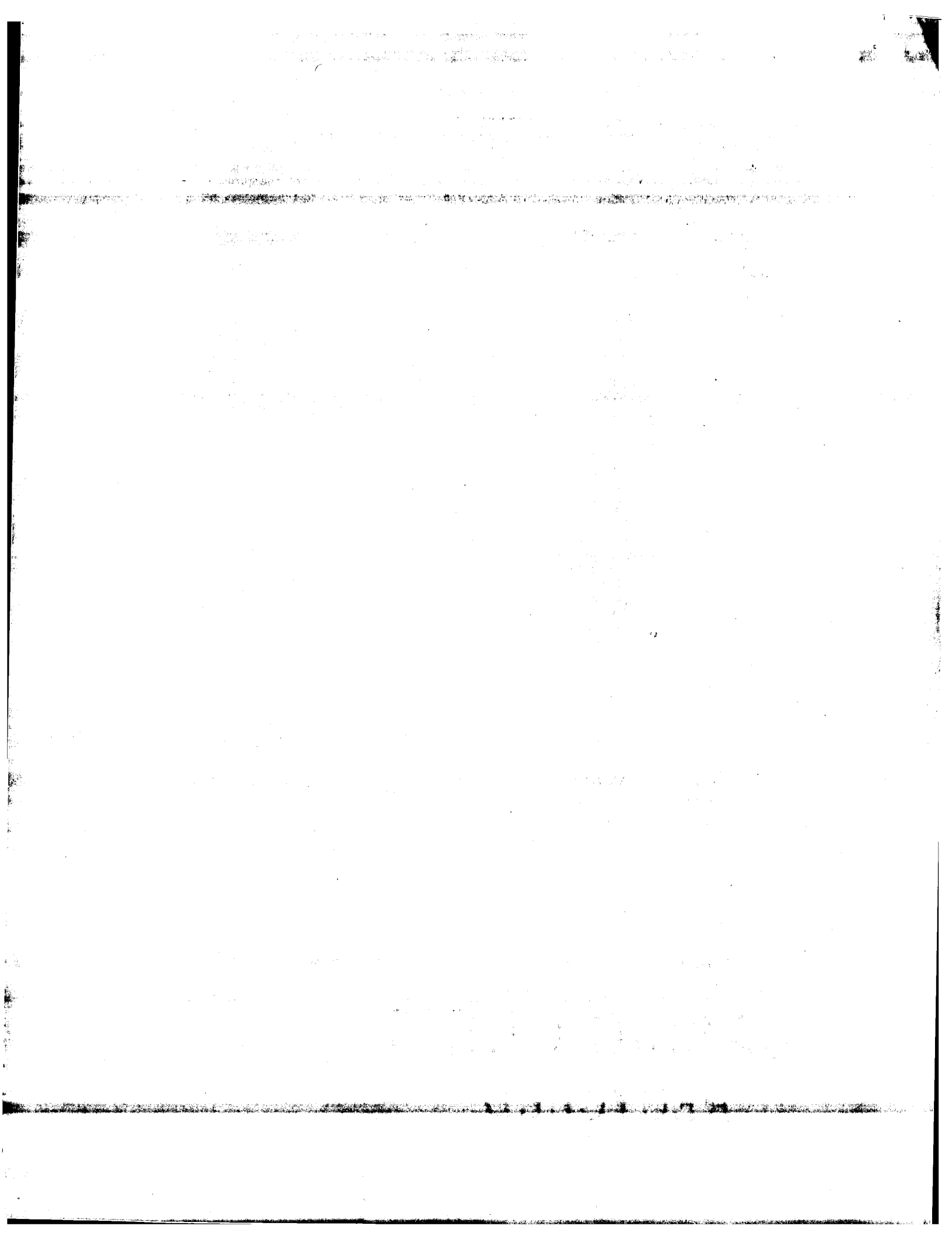
1 521 579

- (21) Application No 38348/76 (22) Filed 16 Sep. 1976 (19)
 (31) Convention Application No 614018 (32) Filed 17 Sep. 1975 in
 (33) United States of America (US)
 (44) Complete Specification published 16 Aug. 1978
 (51) INT CL² B29D 7/24 27/00
 D01D 5/26
 (52) Index at Acceptance
 B5B 230 283 35Y 360 363 365 38Y 408
 412 422 611 614 64Y 799



(54) "PROCESS FOR STRETCHING A THERMOPLASTIC MATERIAL"

- (71) We, BIAx-FIBERFILM CORPORATION, a corporation organised and existing under the laws of the State of Wisconsin, United States of America, of 1066 American Drive, P.O. Box 512, Neenah, Wisconsin, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-
- This invention relates to a process for stretching a thermoplastic polymer or blend thereof, and more particularly to a process for stretching such a film to produce an opaque, low density, porous sheet of film.
- Such an opaque, low density, porous sheet or film is useful as a printing substrate, such as synthetic paper; as a substitute for leather; as a highly fibrillated sheet which can easily be shredded into fine fibrils to be used as substitutes for paper-making pulps, or as a filter material, such as battery separators.
- Many polymeric materials or especially blends thereof are known to undergo fibrillation and/or pore formation upon stretching or drawing. A number of such blends are described in U.S. patents Nos. 3,697,367 and 3,511,742. Such pore formation may result from different causes, such as separation of phases of incompatible polymer blends, or separation of inorganic polymer fillers such as clay or titanium dioxide from the polymer matrix due to stress concentration. Most common in such systems is that the maximum pore formation effect occurs at a draw temperature which is relatively low for the particular polymer system. When the same polymer or blend thereof is stretched at higher temperatures, the pore formation diminishes and a denser film results.
- At temperatures where pore formation occurs accompanied by a decrease in density, the draw tension also increases. Draw tension or yield strain also increases with increasing draw rate or operating speed, and reaches the breaking strength of the base film at speeds which are slow and uneconomical for conventional systems used for stretching or drawing of films. Operating a conventional stretching system, such as longitudinal stretching by Goudet rolls and lateral stretching by tenter frames, under tensions which approach the breaking strength of the base film often causes breaks and frequent interruptions of the process. Extrusion speeds are uneconomically slow; for instance, an acceptable draw rate of 200 cm/min in a single longitudinal draw step over Goudet rolls for a 90 wt% polystyrene (See Example 1) would limit the extrusion rate (for a 3' linear die at a draw ratio of 2.0 and a film thickness of 100 micron) to 23.2 lb/hr.
- The processes heretofore advanced for making porous films suffer from the disadvantages of, inter alia, low production rates, low yields and non-uniform quality.
- The present invention provides a process for longitudinally stretching a film of synthetic thermoplastic material which is a thermoplastic orientable polymer or a blend of a thermoplastic orientable polymer with an incompatible second phase which is an incompatible polymer or inorganic material or a polymer matrix having an inorganic filler, the process comprising:
- introducing the said film into a nip of interdigitating rollers having grooves substantially parallel to the axis of the rollers;
 - controlling the velocity of introduction of the film into the said nip to assume and maintain a velocity substantially identical to the rotational velocity of the rollers to thereby longitudinally stretch incremental portions of the film;
 - withdrawing the film from the rollers at a velocity greater than the rotational velocity



of the rollers;
and

(d) collecting the thus formed sheet.

Thus there is provided a process for selective stretching of a film of a synthetic thermoplastic material selected from a thermoplastic orientable polymer or a blend of a thermoplastic orientable polymer with an incompatible second phase which is an incompatible polymer or inorganic material or a polymer matrix, in a station provided with a set of grooved rollers to form an opaque, low density, porous film. The groove pattern of the rollers is generally of a sinusoidal wave wherein the film is stretched in a manner to effect uniform stretching between contact points of the material to produce a material of larger dimension in the direction of stretch.

In accordance with a preferred embodiment of the present invention, there is provided a process for stretching such a film in a first and a second station wherein the first and second stations are provided with sets of rollers having grooves parallel and perpendicular, respectively, to the axis of each set of rollers. The film of synthetic material is stretched in a manner to effect uniform stretching between contact points to produce an opaque, low density, porous sheet.

In a particularly preferred embodiment, a plurality of stations are arranged in a preselect manner, as determined by product requirements, e.g. a multiplicity of sets of rollers having parallel grooves.

The invention will be further described, by way of example only, with reference to the accompanying drawings, wherein:

Figure 1 is a schematic side elevational view of a first station of an apparatus used in the process of the present invention;

Figure 2 is an enlarged view of the film entering the rollers;

Figure 3 graphically illustrates a sinusoidal curve;

Figure 4 is a schematic side elevational view of a second station of the apparatus used in the process; and

Figure 5 is a top view of the second station followed by another first station.

Drive and support assemblies, timing and safety circuits and the like known and used by those skilled in the art have been omitted from the drawings in the interest of clarity.

Referring to Figure 1 illustrating the first station of the apparatus, there is provided a supply roll 10 on which is mounted a film 12 of a synthetic thermoplastic material selected from a thermoplastic orientable polymer or a blend of a thermoplastic orientable polymer with an incompatible second phase selected from an incompatible polymer or inorganic material. The film 12 is coursed between a nip 14 of a pair of rollers 16 having a plurality of tips 18 forming grooves 20 parallel to the axis of the rolls 16, as seen in Figure 2. The film is maintained against the lower grooved roller 16 by a pair of press rollers 22 to ensure that the velocity V_1 of the film 12 is substantially identical to the surface velocity V_1 of the grooved rollers 16. The grooves 20 of the rollers 16 are intermeshed like gears, as known to those skilled in the art. As the film 12 enters the nip 14, the film 12 assumes the shape of the grooves 20 and is stretched (See Figure 2) by a factor determined by the length of the sinus wave "l" (See Figure 3) of the groove divided by the distance "w" between contact points of each respective groove tip, since the film 12 is prevented from slipping by the press rollers 22 to prevent the introduction of more material, as is more commonly practices in the corrugating art.

The draw ratio (l/w) is calculated by the following equation:

$$l/w = 1/\pi \int_0^{\pi} \sqrt{1 + a^2 \cos^2 x} \, dx$$

where a $\pi d/w$; and d = groove depth. Thus for d/w ratios of 1.0, 0.75, and 0.5 the draw ratios are 2.35, 2.0 and 1.6, respectively. The longitudinal draw rate is defined by the following equation:

$$\text{draw rate} = V_2 - V_1$$

where V_1 = film velocity entering rollers; and

V_2 = film velocity leaving rollers.

The Actual Draw Rate (ADR) for longitudinal or lateral stretching is calculated by the following equation:

$$\text{ADR} = \frac{(\text{draw ratio} - 1)V}{4d/w\sqrt{R/d} - 1/4}$$

where,

d = groove depth in cms;

w = distance between tips in cms;

l = length of sinusoidal wave in cms;

19510 3122A.10

31101 0114

the draw ratio = $1/w$;

V is the velocity of the film entering the nip of the rollers in CMS/MIN; and
R is the radius of the rollers in cms.

The roller speed in cms/MIN can be calculated as follows:

5

$$V = \text{ADR} \cdot 4d/a \cdot R/d \cdot 1/4$$

draw ratio : 1

5

Thus if the critical ADR for a composition operating at about 80% of breaking tension is 100 cm/min., and $d/w = 1$, draw ratio is 2.25, R is 10 cm. and $d = 0.3$ cm., then $V_1 = \text{ADR}$.
18.41 = 1841 cm/min., which is 18.41 times faster than permissible with Goudet rolls. For a 6 inch wide film die making 4 mil. film, an extrusion rate of 565 lbs/hr. can be obtained vice 30.4 lbs/hr.

10

10

The film 24 after passage through the nip 14 of the rollers 16 is pulled away by a pair of tension rollers 26 having a surface velocity V_2 greater than the surface velocity of the rollers 16, but not greater than a factor of the draw ratio affected in the nip 14 of the rollers 16. In accordance with the present invention, the length of film is therefore increased by this factor.

15

15

It is noted that the film does not undergo narrowing while being longitudinally stretched or extended, as is the case with conventional roller systems. It will be apparent to one skilled in the art that the film may sequentially pass through a plurality of pairs of grooved rollers 16 to further stretch lengthwise the film 24.

20

20

Referring now to Figure 4, the longitudinally stretched film 24 from the first station is introduced into a nip 26 formed by a pair of rollers 30 having a plurality of tips 32 (see Figure 5) forming grooves 34 parallel to the circumference of the rollers 30 in a second station of the apparatus. The film 24 is caused to be coursed into the nip 28 by a pair of press rollers 36 which holds the film 24 against the lower roller 30 to thereby prevent the film 24 from narrowing prior to introduction. Once in the nip 28, the film 24 assumes the shape of the groove pattern (See Figure 2) and becomes laterally stretched by a factor of the draw ratio determined in a manner similar to the draw ratio discussed with reference to Figure 1.

25

25

The crimp pattern is flattened-out by stretching the sheet 36 laterally by means of tenter clamps or curved Mount Hope (Registered Trade Mark) rollers 38.

30

30

In the second station, i.e., lateral stretching, the sheet 36 is wound up at about the same velocity as the feed velocity with the product being collected on a roll 40. For best results, the longitudinal and lateral stretching steps are repeated alternately through multiple passes each having a relatively low draw ratio, until the total permissible draw ratio is reached. The number of longitudinal and lateral passes, as well as the extent of the stepwise draw ratios, can be chosen so that a final film is obtained with the desired properties. Figure 5 illustrates the film 36 being further coursed into a set of rollers having grooves parallel to the axis for further longitudinal stretching.

35

35

The invention will be further described with reference to the following illustrative Examples, of which only Examples IV to XI actually illustrate the process according to the invention.

40

40

Example I

90 parts by weight of isotactic polypropylene (commercial Profax 6423) of melt flow rate of 6 gram/10 min. and 10 parts by weight of polystyrene (Dow's Styron 686) were dry blended and extruded as a mixture into a homogenous film through a 6 inch flat film die at 450CF. on a rotating metal drum to form a film 100 microns thick and having a 93 gram/m² basis weight. "Profax" and "Styron" are Registered Trade Marks. The film appeared clear with a slight haze. Strips 6 inches long and 1 inch wide were stretched in an Instron (Registered Trade Mark) tensile tester equipped with an oven to heat the samples between the clamps. Samples were stretched to break at various temperatures as shown in Table 1. The yield strain, which stayed approximately constant between 20 and 300% elongation, was measured at the point of 200% elongation. During stretching, the samples necked down to a width of about $\frac{1}{4}$ inch. Yield strain was measured in:

45

45

50

50

55

55

$$\frac{\text{gram/linear m strain}}{\text{gram/m.}^2 \text{ basis weight of original film}}$$

60

60

From Table 1 it may be seen that at low temperatures where void formation due to internal fibrillation occurred (which produces lower density and opacity), the yield strain is quite high and close to the level of the breaking strength. At higher temperature, yielding occurred at a lower strain, breaking strength and elongation at break was higher, but the opacifying effect was lost.



THE UNIVERSITY OF CHICAGO
LIBRARY

Table I

	Stretch Tem- perature °C.	Yield Strain m.	Breaking Strength m.	Elonga- tion at break %	Density g/cm. ³	Appear- ance	
5	25	7400	8100	380	0.62	white, opaque	5
	40	6300	9200	430	0.66		
	60	4600	9400	470	0.75	slightly opaque	
	80	2350	12900	550	0.88	hazy	
10	100	1950	13400	650	0.193	almost clear	10

clamp span distance: 10 cm
stretch rate: 40 cm/min = 400%/min.

Example II

The base film of Example I was stretched as in Example I at 25°C to form a low density opaque film. The stretch rate was varied to show the effect of stretch rate to yield strain. At a stretch rate of 200 cm/min. or 2000%/min. the yield strain increased so much that it came close to the breaking strength indicating that a commercial process under these conditions would become critical to operate. Data are summarized in Table 2:

Table 2

	Stretch rate cm/min.	yield strain m.	breaking strength m.	Elongation break %	density after stretch g/cm.	
20						20
25	40	7430	8120	380	0.62	25
	100	7640	8100	390	0.62	
	200	7920	8030	250	0.58	
	300	immediate break,	no stretching	3535	3535	

Example III

Example II was repeated at an oven temperature of 60°C. It can be seen from Table 3 that yield strain increased as the stretch rate increased, somewhat higher stretch rates being possible than at 25°C., density being higher and opacity somewhat lower than at 25°C.

Table 3

	Stretch rate cm/min.	yield strain m.	Breaking strength m.	Elongation at break %	density g/cm. ³	
35	40	6300	9200	470	0.75	35
	100	6450	9250	430	0.75	
	200	7510	9050	380	0.68	
40	300	8150	8850	380	0.65	40

Example IV

Film as produced in Example I was introduced through a pair of grooved rollers (as shown in Figure 1). The grooves had an approximate sinusoidal shape and were 3mm. deep and 3mm. apart and produced a draw ratio of about 2. When the film was stretched to conform with the shape of the grooves, 8 groove tips simultaneously engaged the film. The film was introduced into the nip of the intermeshing grooved rollers rotating at 60 RPM to produce a feed velocity V_1 of 1914 cm./min. and was wound at 3828 cm./min. The actual film draw rate was 120 cm./min. The film had opaque lines at 3 mm. intervals corresponding to the contact points with undrawn clear sections inbetween.

Example V

A set of grooved rolls having grooves 1 mm. deep and 2 mm. apart (draw ratio of 1.4) rotating at 180 RPM = 5742 cm./min. stretched a film (as produced in Example I) and was wound at 8039 cm./min. This produced an actual draw rate of 162 cm./min. The resulting film showed opaque white lines about every 2 mm. with clear undrawn section inbetween. This Example illustrates that stretching can be effected at low draw ratios at high operating speeds.

Example VI

The stretched film of Example V was passed through the grooved rollers of Example IV three more times under identical conditions to produce a total draw ratio of 3.84. The film showed groove marks but the clear sections disappeared. The film had a tensile strength in the stretch direction of 27500 m. and an elongation at break of 32% indicating that stretching was almost complete. The basis weight of the opaque sheet was 26 grams/m² at a thickness of 40 micron, and thus the density was 0.65 grams/cm³.

Example VII

The stretched film of Example VI was passed through the grooved rollers two more times as described in Example VI. The film started to tear due to overdrawing and appeared to be highly fibrillated and possessed almost no strength in the cross direction. Strips $\frac{1}{4}$ inch wide were cut at right-angles to the stretch direction and 5 grams of such clippings were stirred in a high speed Waring blender with 500 milliliters of water for 5 minutes. The film disintegrated into a finely fibrillated pulp consisting of fibres of about 0.1 micron to 50 microns thick and 100 to 6000 microns long.

Example VIII

Polypropylene (Profax 6423 of the Hercules Powder Co. Inc.) was compounded in a Banbury mixer with 10% by weight of "OX-1" clay of the Freeport Kaolin Co. with the molten mixture thereafter pelletized in a conventional pelletizing extruder. OX-1 clay is a grade which has been treated to be compatible with hydrofobic resins such as polyolefins as described in U.S. Patent No. 3,697,474. The blend was extruded as described in Example I to a film 150 micron thick and 6 inches wide. The film appeared hazy, but almost transparent, since the refractive indices of clay and polypropylene do not significantly differ. The film, when stretched cold, became opaque due to a fibrillating effect initiated by the dispersed clay particles accompanied by a decrease of density of the opaque film indicating the formation of voids. When the film was stretched at high temperature, stretch tension decreased and opacity was not formed.

Stretch Temperature °C	Yield Strain m.	Breaking Strength m.	Elongation at Break %	Density gm/cm ³
25	11570	19600	650	0.66
60	8070	25700	750	0.82
110	4060	27650	850	1.06

(Instron conditions as in Example I).

clamp span distance 10 cm., stretch rate: 40 cm./min.

Example IX

The polypropylene/clay film of Example VIII was drawn through the nip of a pair of grooved rollers (as described in Example IV) having grooves 3 mm. deep and 3 mm. apart rotating at a speed of 60 RPM = 1914 cm./min. The resulting film had opaque lines every 3 mm. corresponding to the groove contact points with clear sections inbetween. The draw ratio at this groove shape was about 2.0, and the film was wound at twice the feed velocity. The actual draw rate was 120 cm./min. The speed of the rollers was generally increased to 200 RPM of 6384 cm./min. whereat the film started to rupture severely along the opaque lines. The actual draw rate at this point was 399 cm./min.

Example X

The polypropylene/clay film of Example VIII was drawn through the nip of a pair of grooved rollers having grooves parallel to the roller axis 1 mm. deep and 2 mm. apart (as described in Example V) and subsequently through a pair of rollers having grooves 1 mm. deep and 2 mm. apart vertical to the roller axis. This resulted in a longitudinal stretch and subsequent lateral stretch by a factor of 1.4 in each direction. The second pair of grooved rollers was operated at 84 RPM. Before winding, the sheet was flattened out over a series of curved Mount Hope rolls. Longitudinal and lateral stretching was repeated two more times. The resulting film was then stretched biaxially 2.7 times in each direction and was then completely opaque. After calendering between a pair of smooth rollers at 60°, the basis weight was 21 gram/m², reduced from an original 155 gram/m². Groove marks at right angles were still visible and gave the opaque film a woven cloth-like appearance.

Example XI

A polyethylene terephthalate of 0.9 intrinsic viscosity and a general purpose polystyrene of melt index 12.0 were blended in a weight ratio of 7 to 3 and extruded through a flat film die to form a 16 mil film of 505 gram/m² basis weight. A 10 x 10 inch piece was passed through a pair of grooved rollers having grooves parallel to the roll axis 3 mm. deep and 3 mm. apart. After the line embossing pattern had been flattened out by a pair of smooth calender rollers, the sheet had a size of 10 x 16 inch, indicating an actual draw ratio of 1.6. Subsequently the sheet was passed through the grooved rollers (at 30 RPM) turned 90 degrees, thus applying a biaxial stretch ratio of 1.6 x 1.6. The process was repeated once more to a total biaxial draw ratio of 2.56 x 2.56. The sheet was then drawn out to a size of about 26 x 26 inch, appearing highly opaque and having a basis weight of 76 gram/m². The sheet was then treated with boiling toluene to dissolve the polystyrene. The resulting polyester sheet was porous, and had a fibrous structure and a soft, leather-like feel.

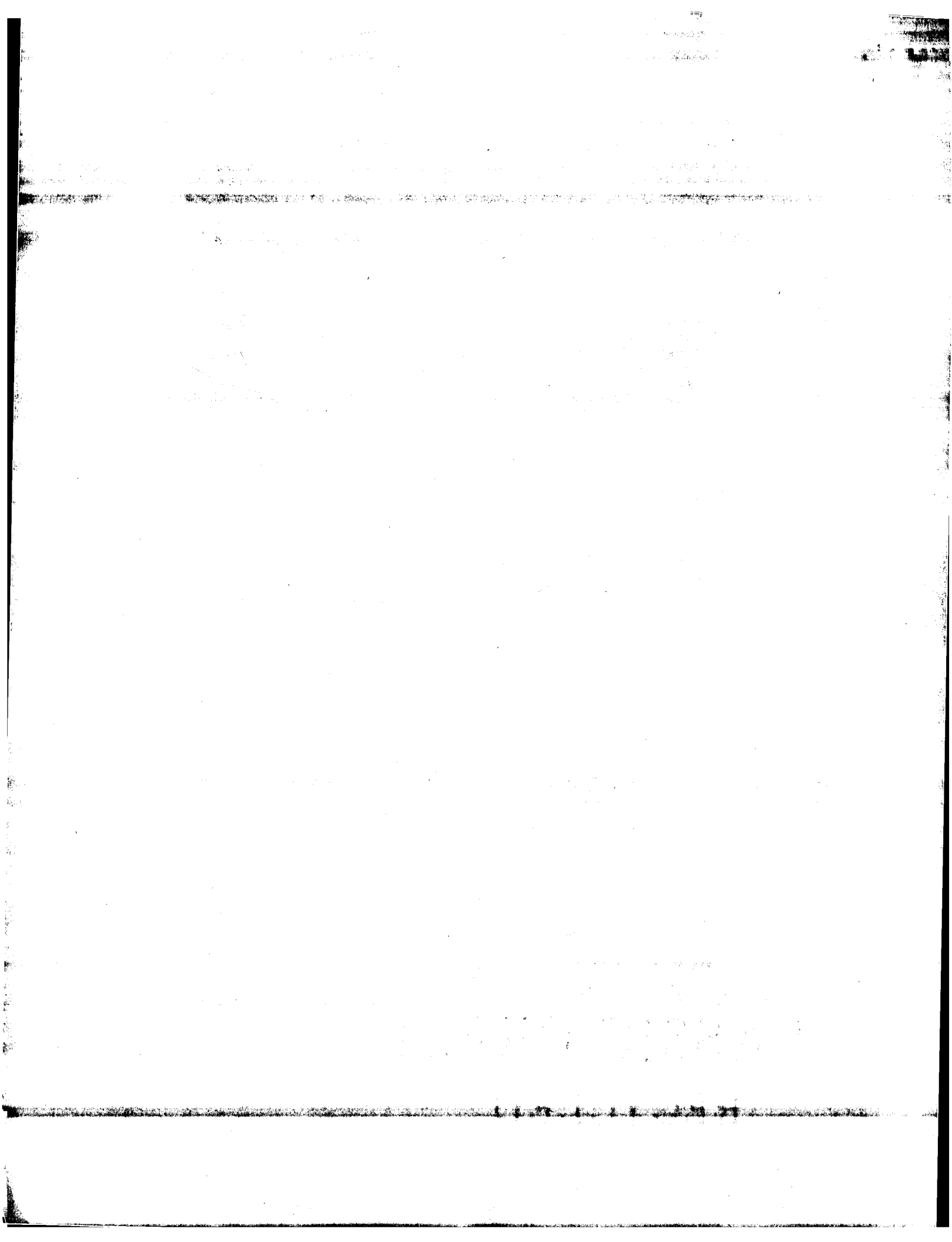
While the present invention has been described with reference to the passage of a film through a first longitudinal stretching station and thence a lateral stretching station, it is apparent that such stations may be altered with the film being first introduced into a lateral stretching station. Further, the film may be subjected to a plurality of longitudinally oriented stretching rollers. It will also be appreciated that the grooves need not be exactly parallel or perpendicular as long as the grooves intermesh.

It will be appreciated that the grooved roller drawing permits multiple simultaneous draw necks which allow for further actual speed where draw tension is high. At high draw tension (low temperature), the fibrillation phenomenon occurs which is highly desirable for porous films. Additionally, the grooved roll drawing permits a partial draw (draw below the natural draw ratio) in multiple stages thereby further reducing the actual draw rate and increasing the production rate. Still further defects in the base film, e.g. gels or holes, are carried through the grooved roll drawing with no interruption in the process as distinguished from drawing in conventional Goudet and tenter frame drawing wherein such defects usually result in breaks and the necessity for subsequent shutdown.

Attention is drawn to our copending application No. 1251/76. (Serial No. 1521183).

WHAT WE CLAIM IS:

1. A process for longitudinally stretching a film of synthetic thermoplastic material which is a thermoplastic orientable polymer or a blend of a thermoplastic orientable polymer with an incompatible second phase which is an incompatible polymer or inorganic material or a polymer matrix having an inorganic filler, the process comprising:
 - (a) introducing the said film into a nip of interdigitating rollers having grooves substantially parallel to the axis of the rollers;
 - (b) controlling the velocity of introduction of the film into the said nip to assume and maintain a velocity substantially identical to the rotational velocity of the rollers to thereby longitudinally stretch incremental portions of the film;
 - (c) withdrawing the film from the rollers at a velocity greater than the rotational velocity of the rollers; and
 - (d) collecting the thus formed sheet.
2. A process as claimed in Claim 1 wherein the withdrawal velocity of step (c) is not greater than a factor of the draw ratio of the said nip.
3. A process as claimed in Claim 1 or 2 wherein steps (a), (b) and (c) are repeated to a point below the break point of the film.
4. A process as claimed in Claim 3 wherein the resulting product is cut into strips and subjected to agitation to form fibres.
5. A process as claimed in any of Claims 1 to 3 wherein the said incompatible phase is contacted with a selective solvent to dissolve the said phase.
6. A process for bi-axially stretching a film of synthetic thermoplastic material which is a thermoplastic orientable polymer or a blend of a thermoplastic orientable polymer with an incompatible second phase which is an incompatible polymer or inorganic material, the process comprising:
 - (a) introducing the said film into a nip of interdigitating rollers having grooves parallel to the axis of the rollers;
 - (b) controlling the velocity of introduction of the film into the said nip to assume and maintain a velocity substantially identical to the rotational velocity of the rollers to thereby longitudinally stretch incremental portions of the film;
 - (c) withdrawing the film from the rollers at a velocity greater than the rotational velocity of the rollers;
 - (d) introducing the said film into a nip of interdigitating rollers having grooves substantially perpendicular to the axis of the rollers;
 - (e) controlling the velocity of introduction of the said nip to assume and maintain a velocity substantially identical to the rotational velocity of the rollers thereby to laterally stretch incremental portions of the film;
 - (f) laterally elongating and withdrawing the film from the rollers at a velocity substantially corresponding to the velocity of introduction; and
 - (g) collecting the bi-axially stretched material.
7. A process as claimed in Claim 6 wherein the steps (a) to (f) are repeated prior to step (g).
8. A process as claimed in Claim 6 or 7 wherein steps (d) to (f) are effected prior to steps (a) to (c).
9. A process as claimed in any of Claims 6 to 8 wherein the said incompatible phase is contacted with a selective solvent to dissolve the said phase.
10. A process as claimed in any of Claims 6 to 8 wherein the said incompatible material is an inert filler and wherein the resulting film is contacted with a solvent to dissolve the said



inorganic filler.

11. A process for stretching a film of synthetic thermoplastic material substantially as herein described with reference to the accompanying drawings.

5 12. A process for stretching a film of synthetic thermoplastic material substantially as herein described in any of the foregoing Examples IV to XI. 5

13. The product of the process as claimed in any of Claims 1 to 12.

10

MARKS & CLERK
Chartered Patent Agents
57-60 Lincolns Inn Fields,
LONDON, WC2A 3LS.

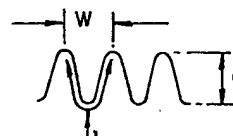
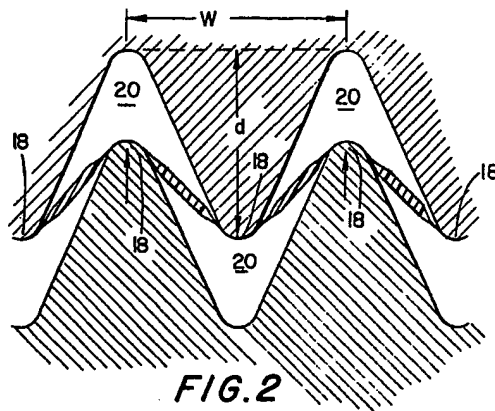
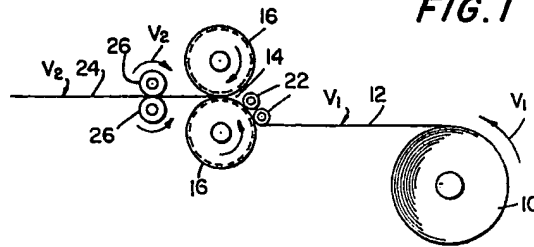
10

Agents for the applicants

the 1990s, the number of people in the world who are under 15 years of age is expected to increase from 1.1 billion to 1.5 billion. The number of people aged 65 and over is expected to increase from 200 million to 400 million. The number of people aged 15 and over is expected to increase from 3.5 billion to 4.5 billion. The number of people aged 15 and over is expected to increase from 3.5 billion to 4.5 billion. The number of people aged 15 and over is expected to increase from 3.5 billion to 4.5 billion.

Journal of Management Education 30(6)

FIG. 1



DRAW RATIO =

$$\frac{l}{w} = \frac{1}{\pi} \int_0^{\pi} \sqrt{1 + d^2 \cos^2 x} dx$$

$$\alpha = \frac{\pi d}{w}$$

FIG. 3

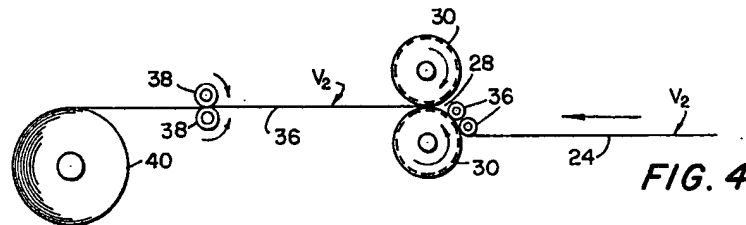


FIG. 4

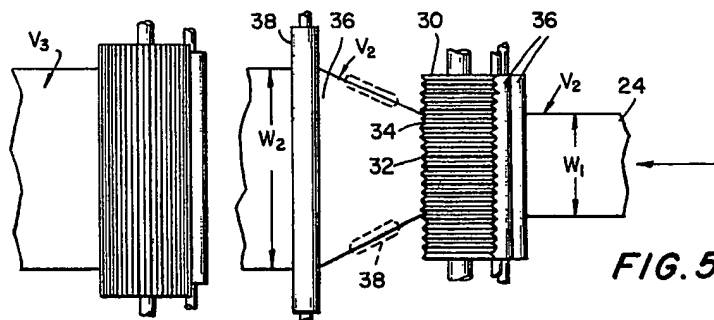


FIG. 5

1. *Chlorophyll a* (Chl *a*)
 2. *Chlorophyll b* (Chl *b*)
 3. *Chlorophyll c* (Chl *c*)
 4. *Chlorophyll d* (Chl *d*)
 5. *Chlorophyll e* (Chl *e*)
 6. *Chlorophyll f* (Chl *f*)
 7. *Chlorophyll g* (Chl *g*)
 8. *Chlorophyll h* (Chl *h*)
 9. *Chlorophyll i* (Chl *i*)
 10. *Chlorophyll j* (Chl *j*)
 11. *Chlorophyll k* (Chl *k*)
 12. *Chlorophyll l* (Chl *l*)
 13. *Chlorophyll m* (Chl *m*)
 14. *Chlorophyll n* (Chl *n*)
 15. *Chlorophyll o* (Chl *o*)
 16. *Chlorophyll p* (Chl *p*)
 17. *Chlorophyll q* (Chl *q*)
 18. *Chlorophyll r* (Chl *r*)
 19. *Chlorophyll s* (Chl *s*)
 20. *Chlorophyll t* (Chl *t*)
 21. *Chlorophyll u* (Chl *u*)
 22. *Chlorophyll v* (Chl *v*)
 23. *Chlorophyll w* (Chl *w*)
 24. *Chlorophyll x* (Chl *x*)
 25. *Chlorophyll y* (Chl *y*)
 26. *Chlorophyll z* (Chl *z*)
 27. *Chlorophyll aa* (Chl *aa*)
 28. *Chlorophyll ab* (Chl *ab*)
 29. *Chlorophyll ac* (Chl *ac*)
 30. *Chlorophyll ad* (Chl *ad*)
 31. *Chlorophyll ae* (Chl *ae*)
 32. *Chlorophyll af* (Chl *af*)
 33. *Chlorophyll ag* (Chl *ag*)
 34. *Chlorophyll ah* (Chl *ah*)
 35. *Chlorophyll ai* (Chl *ai*)
 36. *Chlorophyll aj* (Chl *aj*)
 37. *Chlorophyll ak* (Chl *ak*)
 38. *Chlorophyll al* (Chl *al*)
 39. *Chlorophyll am* (Chl *am*)
 40. *Chlorophyll an* (Chl *an*)
 41. *Chlorophyll ao* (Chl *ao*)
 42. *Chlorophyll ap* (Chl *ap*)
 43. *Chlorophyll aq* (Chl *aq*)
 44. *Chlorophyll ar* (Chl *ar*)
 45. *Chlorophyll as* (Chl *as*)
 46. *Chlorophyll at* (Chl *at*)
 47. *Chlorophyll au* (Chl *au*)
 48. *Chlorophyll av* (Chl *av*)
 49. *Chlorophyll aw* (Chl *aw*)
 50. *Chlorophyll ax* (Chl *ax*)
 51. *Chlorophyll ay* (Chl *ay*)
 52. *Chlorophyll az* (Chl *az*)
 53. *Chlorophyll aza* (Chl *aza*)
 54. *Chlorophyll abz* (Chl *abz*)
 55. *Chlorophyll acz* (Chl *acz*)
 56. *Chlorophyll adz* (Chl *adz*)
 57. *Chlorophyll aez* (Chl *aez*)
 58. *Chlorophyll afz* (Chl *afz*)
 59. *Chlorophyll agz* (Chl *agz*)
 60. *Chlorophyll ahz* (Chl *ahz*)
 61. *Chlorophyll aiz* (Chl *aiz*)
 62. *Chlorophyll ajz* (Chl *ajz*)
 63. *Chlorophyll akz* (Chl *akz*)
 64. *Chlorophyll alz* (Chl *alz*)
 65. *Chlorophyll amz* (Chl *amz*)
 66. *Chlorophyll anz* (Chl *anz*)
 67. *Chlorophyll aoz* (Chl *aoz*)
 68. *Chlorophyll apz* (Chl *apz*)
 69. *Chlorophyll aqz* (Chl *aqz*)
 70. *Chlorophyll arz* (Chl *arz*)
 71. *Chlorophyll asz* (Chl *asz*)
 72. *Chlorophyll atz* (Chl *atz*)
 73. *Chlorophyll auz* (Chl *auz*)
 74. *Chlorophyll avz* (Chl *avz*)
 75. *Chlorophyll awz* (Chl *awz*)
 76. *Chlorophyll axz* (Chl *axz*)
 77. *Chlorophyll ayz* (Chl *ayz*)
 78. *Chlorophyll ayz* (Chl *ayz*)
 79. *Chlorophyll azz* (Chl *azz*)
 80. *Chlorophyll azaa* (Chl *aza*)
 81. *Chlorophyll abz* (Chl *abz*)
 82. *Chlorophyll acz* (Chl *acz*)
 83. *Chlorophyll adz* (Chl *adz*)
 84. *Chlorophyll aez* (Chl *aez*)
 85. *Chlorophyll afz* (Chl *afz*)
 86. *Chlorophyll agz* (Chl *agz*)
 87. *Chlorophyll ahz* (Chl *ahz*)
 88. *Chlorophyll aiz* (Chl *aiz*)
 89. *Chlorophyll ajz* (Chl *ajz*)
 90. *Chlorophyll akz* (Chl *akz*)
 91. *Chlorophyll alz* (Chl *alz*)
 92. *Chlorophyll amz* (Chl *amz*)
 93. *Chlorophyll anz* (Chl *anz*)
 94. *Chlorophyll aoz* (Chl *aoz*)
 95. *Chlorophyll apz* (Chl *apz*)
 96. *Chlorophyll aqz* (Chl *aqz*)
 97. *Chlorophyll arz* (Chl *arz*)
 98. *Chlorophyll asz* (Chl *asz*)
 99. *Chlorophyll atz* (Chl *atz*)
 100. *Chlorophyll auz* (Chl *auz*)
 101. *Chlorophyll avz* (Chl *avz*)
 102. *Chlorophyll awz* (Chl *awz*)
 103. *Chlorophyll axz* (Chl *axz*)
 104. *Chlorophyll ayz* (Chl *ayz*)
 105. *Chlorophyll ayz* (Chl *ayz*)
 106. *Chlorophyll azz* (Chl *azz*)
 107. *Chlorophyll azaa* (Chl *aza*)
 108. *Chlorophyll abz* (Chl *abz*)
 109. *Chlorophyll acz* (Chl *acz*)
 110. *Chlorophyll adz* (Chl *adz*)
 111. *Chlorophyll aez* (Chl *aez*)
 112. *Chlorophyll afz* (Chl *afz*)
 113. *Chlorophyll agz* (Chl *agz*)
 114. *Chlorophyll ahz* (Chl *ahz*)
 115. *Chlorophyll aiz* (Chl *aiz*)
 116. *Chlorophyll ajz* (Chl *ajz*)
 117. *Chlorophyll akz* (Chl *akz*)
 118. *Chlorophyll alz* (Chl *alz*)
 119. *Chlorophyll amz* (Chl *amz*)
 120. *Chlorophyll anz* (Chl *anz*)
 121. *Chlorophyll aoz* (Chl *aoz*)
 122. *Chlorophyll apz* (Chl *apz*)
 123. *Chlorophyll aqz* (Chl *aqz*)
 124. *Chlorophyll arz* (Chl *arz*)
 125. *Chlorophyll asz* (Chl *asz*)
 126. *Chlorophyll atz* (Chl *atz*)
 127. *Chlorophyll auz* (Chl *auz*)
 128. *Chlorophyll avz* (Chl *avz*)
 129. *Chlorophyll awz* (Chl *awz*)
 130. *Chlorophyll axz* (Chl *axz*)
 131. *Chlorophyll ayz* (Chl *ayz*)
 132. *Chlorophyll ayz* (Chl *ayz*)
 133.